# ELECTRICITY HARVESTING FROM WATER VAPOUR USING CHITOSAN FILM

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# ELECTRICITY HARVESTING FROM WATER VAPOUR USING CHITOSAN FILM

by

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#### In the Name of Allah, the Most Gracious and the Most Merciful

Indeed, science is the light, the knowledge that in humans is from Allah SWT. So, there are no words that can be written to express gratitude for the pleasure in the form of such great knowledge. May every knowledge that increases with time always lead us to enhance the acknowledgement of His greatness and blessing.

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# LIST OF SYMBOL

μW	Microwatt
AlPO <sub>4</sub>	Berlinite
BaTiO <sub>3</sub>	Barium Titanate
CdTe	Cadmium Telluride
CIGS	Copper Indium Gallium Diselenide
NH <sub>2</sub>	Amine
OH	Hydroxyl
PBTiO3	Lead Titanate
PZT	Lead Zirconium Titanite
Si	Silicon
SiO <sub>2</sub>	Quartz

# LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
AFM	Atomic Force Microscopy
AC	Alternating Current
DC	Direct Current
DD	Degree of Deacetylation
DSSC	Dye Sensitized Solar Cell
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
HUMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
PVEH	Piezoelectric Vibration Energy Harvesters
RH	Relative Humidity
UV-Vis	Ultraviolet-Visible Spectroscopy

# PENUAIAN TENAGA ELEKTRIK DARI WAP AIR MENGGUNAKAN FILEM KITOSAN

### ABSTRAK

Penurunan rizab petroleum, gas dan arang batu dunia telah membawa kepada pertumbuhan konsensus yang lebih besar mengenai sumber tenaga fosil yang berlebihan yang menyebabkan masalah alam sekitar seperti kesan rumah hijau dan perubahan iklim. Dalam konteks mengekalkan penambahbaikan tenaga mampan, sumber tenaga boleh diperbaharui menawarkan beberapa faedah berbanding dengan tenaga fosil seperti kesan rumah hijau yang mesra alam, lestari dan sifar. Ketersediaan sumber tenaga boleh diperbaharui untuk penjanaan elektrik adalah angin, biomas, surya, panas bumi, air, dan sebagainya. Walau bagaimanapun, potensi keseluruhan dari sumber tenaga boleh diperbaharui adalah agak ketara dan tidak digunakan secara optimum. Oleh itu, satu aplikasi baharu kitosan telah berjaya menjana tenaga elektrik dari pendedahan wap air. Chitosan telah dibuat dalam bentuk filem dengan menggunakan kaedah tuangan larutan yang dihasilkan daripada produk sisa kerang krustasea. Chitosan mempunyai ciri-ciri unik seperti biokompatibiliti yang baik, keupayaan pembentukan filem yang cemerlang, biodegradasi, ketoksikan dan hidrofilik yang boleh digunakan dalam banyak aplikasi. Kehadiran amina dalam struktur kimia cenderung berinteraksi dengan molekul air atau apa-apa analisis di mana kitosan menjadi menonjol dalam medan bahan tenaga. Oleh itu, kajian awal mengenai ujian makmal filem kitosan untuk menuai wap air yang diwakili sebagai kelembapan relatif (RH) dalam lingkungan 30% - 90% pada variasi suhu 20 ° C - 35 ° C telah dilakukan. Hasilnya menunjukkan penjanaan tenaga elektrik mula meningkat dan mencapai keadaan hampir mantap apabila terdedah kepada ≥78% RH pada

pelbagai suhu. Sebagai hasil daripada pendedahan tertinggi 90% RH, filem kitosan 4% menghasilkan tenaga elektrik tertinggi 123.50 µW pada 35 °C selama 24 jam. Ini mengesahkan bahawa proses penuaian melalui interaksi kimia langsung antara kumpulan amin (NH<sub>2</sub>) pada filem kitosan dan molekul wap air (H<sub>2</sub>O) menghasilkan tenaga elektrik yang dibuktikan oleh analisis FTIR. Selepas itu bukti dari proses penuaian, ujian fungsian dilakukan dengan menggunakan persediaan aliran air yang merupakan sebagai model aliran air model sebenar untuk jangka masa yang panjang. Hasil ujian fungsian yang menunjukkan tenaga elektrik filem kitosan mempunyai kecenderongan yang sama dengan pencirian sebelumnya di mana tenaga elektrik tertinggi sebanyak 118.89 µW dihasilkan oleh kitosan 4% selama 30 minggu manakala yang paling lama dipamerkan dari 4.5% sehingga 33 minggu tetapi elektrik tenaganya adalah lebih rendah daripada 4%. Pencirian bahan membuktikan jumlah aglomerasi lebih besar pada filem kitosan yang lebih tinggi daripada 4% yang memberi kesan kepada laluan elektrik namun mewujudkan ikatan kimia yang lebih kuat. Jumlah optimum RH dan suhu boleh digunakan untuk kerja masa depan dalam panel wap air untuk meningkatkan jumlah penuaian tenaga elektrik. Selain itu, tenaga elektrik dari panel wap air boleh digunakan dalam peranti elektrik.

# ELECTRICITY HARVESTING FROM WATER VAPOUR USING CHITOSAN FILMS

## ABSTRACT

The depletion of world petroleum, gas and coal reserves has led to the growth of a greater consensus on excessive fossil energy sources that have caused environmental problems such as the greenhouse effect and climate change. In the context of maintaining sustainable energy improvement, renewable energy sources offer several benefits compared to fossil energy such as eco-friendly, sustainable and zero greenhouse effect. The availability of renewable energy sources for electrical generation is the wind, biomass, solar, geothermal, water, etc. Even so, the overall potential from renewable energy sources is quite significant and has not been utilised optimally. Hence, a new application of chitosan film has been successfully generating electrical energy from water vapour exposure. Chitosan was fabricated in film form by using solution casting method whereby manufactured from the waste product of crustacean shells. Chitosan has unique characteristics such as good biocompatibility, excellent film-forming ability, biodegradation, non-toxicity and hydrophilicity, which can be used in many applications. The presence of amine in chemical structure adores interacting with water molecules or any analytes whereby chitosan becomes prominent in the energy materials field. Therefore, the preliminary study on the laboratory testing of chitosan film to harvest water vapour which represented as relative humidity (RH) in range of 30% - 90% at variance 20  $^{\circ}C$  – 35  $^{\circ}C$  temperatures was done. The results showed the generation of electrical energy was started to increase and to reach an almost steady state when exposed to  $\geq$ 78% RH at various temperatures. As a result of the highest exposure at 90% RH, 4% chitosan film yield the highest electrical energy

of 123.50  $\mu$ W at 35 °C for 24 hours. This verified that the harvesting process through direct chemical interaction between amine groups (NH<sub>2</sub>) on chitosan film and water vapour molecules (H<sub>2</sub>O) generating electrical energy which proved by the FTIR result. Thereafter the evidence from the harvesting process, a functionality test was conducted by using water flow setup which a representative of the actual model water streams under a long period of time. The functionality test results exhibited the electrical energy of chitosan films have a similar trend with the previous characterization whereby the highest electrical energy of 118.89  $\mu$ W was yielded by 4% chitosan for 30 weeks while the longest was exhibited from 4.5% with 33 weeks yet the electrical energy was lower than 4%. The material characterization proved a greater amount of agglomeration on chitosan film higher than 4%, which effecting electrical pathway yet create a stronger chemical bond. The optimum amount of RH and temperatures can be used for future work in water vapour panel to increase the electrical energy harvesting amount. Furthermore, the electrical energy from water vapour panel can be applied in electrical devices.

#### **CHAPTER 1**

### **INTRODUCTION**

### 1.1 Research background

Energy is a foremost human necessity for living. Energy cannot be created nor destroyed but can change to another form. It is indicated that the sources of energy are not limited in number but has limited forms. The most widely used energy sources are fossil energy, namely petroleum, gas and coal. Fossil energy is the most widely available on earth, but the amount nowadays becomes depleted to be fewer. It takes hundreds of millions of years to recycle energy fossil. Nevertheless, the energy demands of human are getting greater, which led to the overexploitation of fossil energy sources.

The depletion of world petroleum, gas and coal reserves has led to the growth of a greater consensus on excessive fossil energy sources that have caused environmental problems such as the greenhouse effect and climate change (Vanek et al., 2008; Solaun and Cerdá, 2019; Cong et al., 2019). In the context of maintaining sustainable energy improvement, several developed countries have reduced fossil energy usage and switch to renewable energy sources. Furthermore, renewable energy sources offer several benefits compared to fossil energy such as eco-friendly, sustainable and zero greenhouse effect (Sekar and Ramasamy, 2015). The availability of renewable energy sources for electrical generation is the wind, biomass, solar, geothermal, water, etc (Akpınar, 2013; Erinofiardi et al., 2015). Even so, The overall potential of renewable energy sources is quite large and has not utilized optimally. The aim of this research is focused on what materials based solutions can offer and show how the improvement or new application of materials properties can lead to energy alternatives that can breakthrough with existing technologies. In terms of alternative means of electricity generation, dramatic fundamental and practical breakthroughs are taking place in the realization of solar cells with high energyconversion efficiency. The improvement of batteries for electric vehicles and the grid is also a major challenge. Key advances in sustainable approaches beyond Li-ion batteries and progress techniques for in situ monitoring and control of redox processes are greatly needed. The conversion of sunlight into fuels and chemicals is also an attractive prospect for energy storage, and major efforts to develop efficient catalysts for both water splitting and CO<sub>2</sub> reduction are underway.

Many difficulties remain, and researchers are working hard to overcome outstanding hurdles by designing new application materials and devices. In order to overcome these problems, a device called water vapour cell was then investigated for harvesting water vapour. A water vapour cell fabricated from chitosan film in the middle, titanium in the bottom layer, patterned silver on the top layer and isolator (ABS) substrate as a kit or cover. A chitosan film in the middle proposed as a material for harvesting water vapour from water energy by direct interaction.

## **1.2 Problem statements**

Renewable energy describes production energy from renewable resources, i.e. solar, wind, hydropower and geothermal derived from sources that are never-ending and can be replenished time after time. Renewable energy has been considered a key role in mitigating climate change, reducing the greenhouse effect and fulfilling electricity high demands which occurred along with the depletion of fossil fuels. Among all renewable resources, solar energy is not always available; the necessity of sunshine to collect light and create electricity is important. Furthermore, it is possible to use only 50% of their actual capacity in the equatorial areas and even less because of the disappearance of the Sun for several months in the poles. Also, when the sky is cloudy, solar radiation is lower, which affect electricity production to become discontinuous and not dispatchable. In addition, solar energy needs a wide collecting area which has a higher cost compared to fossil fuel technologies and

Moreover, wind turbines also have disadvantages which pose a great danger to wildlife. A wind turbine kills about one in three birds per year, but the essential mortality risk is for the bats. Even worse wind energy changes to land and reshapes the landscape settings, which have an impact upon the biological and regional earth surface system. Wind energy has a similar drawback to solar energy in that it is not constant. Although the wind is sustainable and will never run out, wind speed does change. This can cause severe problems for the efficiency of a wind turbine. Another disadvantage of wind turbines is the noise pollution which can be heard from hundreds of meters away depending on the wind direction. This issue is one of the biggest impacts of wind energy.

Even worse for hydropower dams also have far-reaching implications for the environment. Hydropower plants are typically constructed across rivers, and this can interfere with aquatic life and result in their huge-scale devastation. There is a huge probability that the fish or other river animals may find a way into the penstock and eventually into the turbines where they will be exterminated. Construction of dams in specific places needs a large area which interferes with the mating patterns, seasons and breeding areas of the water animals. In addition, it is generally expensive to build up hydropower plants which require maintenance over time.

In order to overcome these problems, a device called water vapour cell is investigated for harvesting water vapour from water energy into electrical energy through direct interaction. A water vapour cell is a device that used chitosan as a material for harvesting water vapour into electrical energy through direct interaction. Chitosan is a natural biopolymer which is obtained from deacetylation of chitin and the second most abundant biopolymer in nature next to cellulose (Corazzari et al., 2015; Inmaculada et al., 2009; Shahidi et al., 1999; Sreekumar et al., 2018). The utilization of chitosan has been used in material for energy fields such as a photovoltaic cell and DSSC (Buraidah et al., 2016; Buraidah et al., 2010; Mohamad et al., 2007; Yusuf et al., 2016; Praveen et al., 2019), fuel cell (A.I and L, 2019; Hari Gopi et al., 2019; Ryu et al., 2019) and batteries (Aydin et al., 2019; Guo et al., 2018; Xu et al., 2019). The other advantage is regarding the production of chitosan, which is obtained from treating seafood waste, especially shells from crustaceans (shrimps, crabs, lobsters, krills, etc). This method makes chitosan becomes a reproducible resource, biodegradable and low cost of production. Thus, chitosan is not harmful to a clean environment when it becomes discarded objects. Therefore, research on chitosan has become something very promising to be developed in order to find a new application.

### **1.3** Research objectives

The research is focused on a study of energy harvesting from water vapour by using chitosan film. The detail objectives are:

- i. To fabricate a water vapour cell which capable of harvesting water vapour into electrical energy.
- To investigate the energy harvesting properties of water vapour cell in harvesting water vapour into electrical energy.
- iii. To test the functionality of water vapour cell into an actual model of water flow setup.

## **1.4** Scope of works

The scopes of this study are divided into three main stages, fabrication of water vapour cell, energy harvesting properties of water vapour cell and the functionality test of water vapour cell. Fabrication of water vapour cell was conducted step by step, which starting with preparing chitosan solution, fabricating chitosan film, patterning the electrode, fabricating the kit and arranging the water vapour cell.

In the fabrication process, the chitosan solution concentrations were varied in the range of 1% w/v until 4.5% w/v which followed by a measurement of viscosity in order to identify the effects toward the material characteristic of chitosan films. Hereafter the chitosan film formed, a kit for configuring each part of water vapour cell was fabricated by using 3D printer while the electrode was patterned previously. Hence, every piece assembled and arranged to form a water vapour cell which then electrically probed by using a multimeter for short-circuit test before use. The energy harvesting properties of water vapour cell stage schemed into two main parts which consist of electrical characterization and material characterization. The water vapour cell was electrically characterized to harvest energy from water vapour by direct chemical interaction. The ideal amount of water vapour was represented by relative humidity (RH) that sufficient to be harvested into electrical energy. The amount of RH was characterized using a climate chamber through the utilization of water vapour cell. In addition, the characterization process was varied within the aspect of relative humidity and temperature. Hence, the electrical characterization of water vapour cell is related to the results of material characterizations.

The material characterization of chitosan films was investigated using Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscopy (FESEM), Atomic Force Microscopy (AFM), and Ultraviolet-Visible Spectroscopy (UV-Vis). Moreover, especially for FTIR characterizations was carried out before and after the exposure of relative humidity to analyse the changes in chitosan films chemical groups while the other material characterization was done before water vapour or relative humidity exposure. The information about the relationship between electrical characterization and the result of material characterizations were utilized to investigate the properties and conversion mechanism of chitosan film in harvesting energy from water vapour. The last stage of this project is a functionality test of the accumulated previous results of water vapour cell. The functionality test was conducted using a water flow setup. A water flow setup is a representative of the actual model from flowing water in reality. This setup generating flowing water which purposed to produce water vapour during the process. The manufactured water vapour cell was then placed over the flowing water that produced water vapour exposure. The results of this experiment were then analyzed to concise functionality test of the water vapour harvesting process.

#### **CHAPTER 2**

### LITERATURE REVIEW

### 2.1 Energy harvesting

Energy has become one of the necessities that can not be separated in all human activities. Energy can be obtained from natural resources such as petroleum that already exist and also utilizing the natural phenomenon as the driving force for energy. However, the imbalance between resources and demand for energy increased the depletion of fossil fuels reserves. On the other hand, there is a separate issue of fossil fuels energy generation which produced problems such as air pollution, ozone layer depletion, water pollution and climate change (Altin and Eyimaya, 2018; Elshkaki and Graedel, 2015; Fant et al., 2016). This issue continues to haunt people which then encourages the researcher to discover another alternative energy from renewable resources to fulfil the energy demands without causing any environmental problems.

Nowadays, alternative energy from renewable resources is known as energy harvesting (Beeby et al., 2013; Chetto and Queudet, 2016). Energy harvesting which also known as energy scavenging is generally defined as a process of extracting, exploiting or gathering the ambient energy from physical or chemical phenomena which present in the environment into electrical energy (Beeby et al., 2013; Chetto and Queudet, 2016). Based on this definition, the flourishing rapidly of harvesting technologies are large solar panels, thermal, vibration and water energy. However, in order to distinguish the similarity in the fundamental process compared to large-scale renewable energy generation, energy harvesting specifically interpreted as a gathering of waste or ambient energy in the environment for the particular use (Tuna and Gungor,

2015). The ambient energy sources used for energy harvesting are light, motion, temperature gradient, electromagnetic radiation, and chemical energy.

The common techniques which have been used to exploit waste energy are: electromagnetic relying on induction, light based on the photoelectric effect, piezoelectric on bases mechanical vibrations, chemical-based on different reactions from the surfaces of the electrodes and thermoelectric depends on the difference of temperature across two materials (Tuna and Gungor, 2015). Most often, it involves powering microelectronic devices due to the amount of energy produced is much smaller, being typically in the range of nanowatts to milliwatts (Tuna and Gungor, 2015). These technologies applicated into small embedded systems which particularly suitable for small power, such as wireless sensor nodes and cyber-physical systems (Tuna and Gungor, 2015).

As for example is a smart indicator for highways. A wireless sensor embedded in the road to measure its surface environment such as the temperature and humidity of the surrounding air. The sensor transmitted the information to a gateway node which collected effectively for real-time measurements in order to plan patrols and salting operations which at that time forwarded the information over the internet. Hence, the power source of that sensor can be supplied from a device which harvesting energy from vibration in roads, solar, wind or thermal energy which present in that environment (Tuna and Gungor, 2015). Each technique has been considered as a prominent research field and continues for further development which in particular has been expanded at a rapid pace. This pattern has directed the special attention on the energy harvesting technique and material developments which have characterized as highly reliable, practical and efficient, low-cost production and eco-friendly (Beeby et al., 2013; Chetto and Queudet, 2016).

Simultaneously, the utilization of energy harvesting technique is required particular properties which depend on the typical materials used. Overall, the selected materials must have abundant availability on earth and can be recycled according to the cycle of technology used, as well as ensuring long-term sustainability required a clean and affordable process (Chetto and Queudet, 2016). Yet, many difficulties remain, which led to the researchers for surpassing the outstanding hurdles, scheming improved materials and devices. Therefore, the sustainable materials and technology development for common alternative energy resources such as solar energy, thermal energy, vibration energy and water energy are discussed furtherly into several sections.

#### 2.1.1 Solar energy harvesting

Solar energy is radiating light and heat from the sun which harvested using several technologies such as solar heating, solar thermal energy, solar architecture, molten salt power plants, artificial photosynthesis and photovoltaics (Husain et al., 2018). This kind of sources is ever-evolve technologies which are broadly characterized as either active solar or passive solar depending on how the occupation and distribution of solar energy or conversion into electrical energy. The utilization of concentrated solar power, solar water heating and photovoltaic systems harvesting the energy are included as active solar techniques.

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Nowadays, the harvesting of solar energy using solar cells is accomplished with the principle of absorption of photons from excited electrons by the semiconductor material. Once excited, the electrons can either scattered its energy into heat and return to the orbital or move towards the electrode and generates electricity. The illustration of the process is depicted in Figure 2.1.



Figure 2.1 Photovoltaic effect illustration (Sarkar and Rahman, 2018)

Generally, these phenomena explained as the photovoltaic effect, which is closely related to the photoelectric effect. The core distinction is that the term photoelectric effect is usually used when light hits a material with the emission of electrons or other free carriers while the photovoltaic effect is the creation of electrical energy between to layers of a semiconductor slice whereby the conductivities are opposite, upon exposure of a light stream (Tobin et al., 2011). At present, solar cells are divided into three generations. The first generation is silicon-based solar cells, the second generation is thin film-based solar cells, and the third generation is organic solar cells. First and second-generation solar cells use the photovoltaic effect, which means the process of producing electrical energy rests on the semiconductor material used. Whereas the third generation solar cells use photoelectrochemical principal.

The first and second-generation were typically used semiconductor from single crystalline silicon, followed cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), and amorphous thin-film silicon. Noteworthy, p-n layers or multijunction structure are required for semiconductor to be used and composed from the same materials, commonly the material was doped by adding particular impurity atoms. The n-type is obtained by doping silicon with elements from pentavalent impurity atoms that share an excess of valence electrons compared to the surrounding atoms.

On the other hand, the p-type semiconductors are obtained by doped with trivalent impurity atoms which resulting in the valence electrons are one deficit compared to the surrounding atoms. Once p-type and n-type semiconductors are connected, the positive charges or holes diffused from p-type to n-type and the contrary with the negative charges or electrons, therefore, the diffusion produced an additional positive region at the n-type boundary and a more negative region at the p-type boundary which illustrated in Figure 2.2.



Figure 2.2 An illustration of electron and holes movements (Al-Alwani et al., 2016)

However, other materials can be used whereby the chemical bonds of the doped materials are crucial for electricity production. Solar energy which absorbed by semiconductor at the p-n junction excited an electron from the valence band to conduction band through the bandgap to produce an extra mobile electron and hole. The resulting electron field creates the electron and hole flow to the n-type and p-type material respectively in which the separation of the negative and positive charges over the junction is termed as a voltage (Al-Alwani et al., 2016). The difference lies with the usage of electrolytes in third-generation solar cells. Dye-Sensitized Solar Cell (DSSC) is a pioneer of third-generation solar cells discovered by M. Gratzel at EPFL in 1991. In contrast to conventional solar cells, DSSC is photoelectrochemical solar cells that use an electrolyte as a charge transport medium. Therefore DSSC is also called the first breakthrough in solar cell technology since silicon solar cells (Halme, 2002). DSSCs also receive special attention in solar cells compared to solar cells that use silicon. This is caused by the process of making DSSC that are simple, inexpensive and result in high efficiency (Tobin et al., 2011).

There are four main components in DSSC namely photoanode, dye, electrolyte and counter electrode (CE). These components play an important role in converting sunlight to electricity. The operation principles of DSSC is shown in Figure 2.3. Unlike the p-n silicon solar cells, in the DSSC, photon light is absorbed by a dye attached to the surface of the titanium dioxide (TiO<sub>2</sub>) which the dye acts as an electron donor while the TiO<sub>2</sub> layer acts as an electron acceptor or collector (Chiang et al., 2013). The electrons from the HOMO (Highest Occupied Molecular Orbital) level of dye molecules are excited to a higher energy level of LUMO (Lowest Unoccupied Molecular Orbital) when the dye molecule absorbs photons with the appropriate energy, similar to the chlorophyll function in plant photosynthesis (Halme, 2002).



Figure 2.3 Principles of DSSC (Al-Alwani et al., 2016)

The energy difference of HUMO and LUMO level is equivalent to the bandgap in inorganic semiconductors whereby they determine the production of photocurrent from DSSC. Furthermore, the collected electron in TiO<sub>2</sub> exited from valance band into conduction band leaving an oxidized state into the dye and moving through the conducting oxide layer and external load to the counter-electrode (platinum). The electron moved to electrolyte which contains triiodide ( $I_3^-$ ) to produce iodine molecules ( $I^-$ ) through redox process in order to share the electron and restore the original state of dye after donating the excited electron to TiO<sub>2</sub>. DSSC is unable to compete with previous generation solar cells because the resulting efficiency is 10 % -14 % which lower than the previous generation solar cells. One drawback of this sensitized dye solar cell is its low stability, mainly due to degradation and leakage in the liquid electrolyte used (Al-Alwani et al., 2016). This makes scientists are still looking for organic solar cells with high efficiency.

## 2.1.2 Thermal energy harvesting

The history of thermal energy, known as thermoelectric, began with the discovery of German scientist Thomas Johann Seebeck in 1821. His experiment made a series connecting copper and iron, and between the two metals, the compass needle was placed. A phenomenon of moving the compass needle occurs when the metal side is heated due to a displacement of electric charge on the metal resulting in a magnetic field. This phenomenon became known as the Seebeck effect (Pennelli, 2014). Jean Charles Peltier in 1834, experimented to see the opposite of a phenomenon inspired by Seebeck's discovery. Two metals connected to electricity conducts heat absorption at the series connection and releases heat at the parallel connection, which illustrated in Figure 2.4. This heat release and absorption are mutual turns around once the direction of the current is reverse which later was known as the Peltier effect (Pennelli, 2014). The Seebeck and Peltier effect illustrated in Figure 2.4.



Figure 2.4 Principles of Seebeck effect and Peltier effect (Twaha et al., 2016)

Emil Lenz in 1838 proved that the Peltier effect could be used to freeze water into ice or melt ice into the water using the direction of heat flow. This result concluded that heat flow could be absorbed or rejected depend on the direction of electrical current. Twenty years later, around 1851, William Thomson gave a comprehensive explanation of the relationship between the Seeback effect and the Peltier effect with thermodynamics. The Peltier Coefficient is the multiplication of the Seebeck coefficient. Thomson finally issued a third effect known as the Thomson effect. The heat can be absorbed or created flowing inside the material, which also proportional to the direction of the electric current flowed (Cai et al., 2019). This comparison constant is called the Thomson coefficient, which is thermodynamically related to the Seeback coefficient. The Seebeck, Peltier and Thomson effect later became the basis for the development of thermoelectric technology. Metals were the initial focus of thermoelectric research, but no significant achievements were made because Seebeck's metal coefficient was too low. Until the 1950s, it benefited from the development of semiconductors so that it could develop rapidly. Thermoelectric is a device to convert temperature changes into a potential difference and vice versa. The temperature gradient that causes the heat carrier and charge (electrons or holes) tend to diffuse through the conductor, from heat to cold sources obtained by placing the material between the heat source ( $T_H$  temperature) and the cold heat source ( $T_C$  temperature) (Tobin et al., 2011). The difference in potential V was generated due to the consequences of diffusion charge carriers that depend on hot and cold material extremities (Twaha et al., 2016). The basic structure of a cell thermoelectric generator is made of two material junctions with the difference doping by placed in series for electrical perspective and parallel for thermal is schematically shown in Figure 2.5.



Figure 2.5 Schematic of the thermoelectric cell (Pennelli, 2014)

#### 2.1.3 Vibration energy harvesting

In 1756, German physicist Franz Aepinus discovered a strange phenomenon, which is a material that when heated or cooled can produce electrical voltage using a Tourmaline as material which originating from East Africa, Sri Lanka and Pakistan. Charles-Augustin de Coulomb assumed that electricity could be generated by applying pressure to the material hereafter that Rene-Just Hauy and Antoine Cesar Becquerel tried to prove Coulomb's assumptions that ended with failure. Meanwhile, Pierre Curie and Jacques Curie proved that Coulomb's assumptions were correct in 1880 using Rossel, tourmaline, quartz and salt materials to generate electricity when under pressure. Hence, this phenomenon is called piezoelectric or better known as the piezoelectric effect. One year later, Gabriel Lippman stated the reverse effect of the piezoelectric (reverse piezoelectric effect) when the material is connected to electrical charge produce changes in dimensions and pressure. Inside the piezoelectric material, there are heaps of positive and negative charges even though the crystal structure is not symmetrical. The working principle of piezoelectric material is shown in Figure 2.6.



Figure 2.6 Principle of piezoelectric material (Sze and Ng, 2006)

Meanwhile, the normal times (before being pressed) charge on the piezoelectric material is balanced (Horiuchi et al., 2018). When pressure is applied, there is a shift in charge where the negative charge will go to the anode, and the positive charge will go towards the cathode to produce an electric voltage (Sze and Ng, 2006). The reverse piezoelectric effect is when a piezoelectric material has flowed electric current so that changes in dimensions and produce pressure (Sze and Ng, 2006). The working principle of the reverse piezoelectric effect is shown in Figure 2.7.



Figure 2.7 Principle of the reverse piezoelectric effect (Horiuchi et al., 2018)

The main disadvantage of this piezoelectric harvesting is low energy conversion efficiency rate, slow technology progression and limited applications. Moreover, piezoelectric harvesting needs to be operated at a constant amount of heat source which needs more research about the utilization of the piezoelectric harvesting technologies.

#### 2.1.4 Water energy harvesting

Harvesting water energy which called hydropower refers to technology that converts water into electrical energy from water streams, waterfalls, ocean waves and water storage in the form of the dam. have several sources of water, including streams, waterfalls, ocean waves and water storage in the form of a dam. (Kaunda et al., 2014; Akpınar, 2013). As one of the applications of green technology, hydropower produces less pollution compared to other generating technologies (Akpınar, 2013; Power et al., 2014). The principle of this technology is to use mechanical energy from water currents to turn turbines which will later be converted into electrical energy.

Hydropower is divided into four categories, namely conventional hydroelectric, run-of-the-river hydroelectricity, small hydro projects, micro-hydro projects, and pumped-storage hydroelectricity. Conventional hydroelectric is a hydropower technology based on the potential energy of water from the dam called Hydroelectric Power Plant (Yuce and Muratoglu, 2015). In contrast to Conventional hydroelectric, run-of-the-river hydroelectricity converts river kinetic energy without making the dam (Yuce and Muratoglu, 2015). The Small hydro projects category for power plants with a capacity of 10 MegaWatts, micro-hydro projects for power plants with a capacity of several KiloWatts, while pumped-storage hydroelectricity is only used when electrical energy is needed (Yuce and Muratoglu, 2015). The utilization of water is very important to drive turbines which are specifically designed depending on the amount of flowing water that could flow to operate the turbine. Turbine is equipment that consists of several turbine inlet water supply equipment, including a blade (runner), rapid pipe (penstock), turbine house (spiral chasing), main valve (inlet valve), loose pipe (draft tube), safety device, shaft, bearings (bearings), and electricity distributors (Kaunda et al., 2014).

According to the momentum of the turbine, water can be divided into two groups, namely reaction turbines and impulse turbines. The reaction turbine works because of water pressure, while the impulse turbine works because of the speed of the water that hits the blade. The working principle of the Reaction Turbine, namely the blades (runners) of the Francis turbine and propeller, function as road blades, the position of the blades is fixed (cannot be moved) (Kaunda et al., 2014).

The blades on the Kaplan turbine function as road blades, the position of the blades can be moved (on their axes) regulated by the servo motor manually or automatically in accordance with the opening of the blade (Kaunda et al., 2014). The process of reducing water pressure occurs both on the blades of the set and blades of the road (runner blade). The working principle of the Pelton Turbine is different from the reactor turbine. The blades in the shape of a bowl function as road blades, their position is fixed (immovable) (Kaunda et al., 2014). The rotation of the turbine will produce mechanical energy which will turn the generator into electrical energy. The difference clearly is shown in Figure 2.8.



Figure 2.8 A schematic of impulse and reaction turbine (Polisetti et al., 2017)

The weakness of water energy harvesting technologies is environmental impacts, reservoir construction and hydrology dependent. Hydropower facilities can affect land use, homes, and natural habitats in the dam area while the construction of surface reservoirs has slowed considerably in recent years. Building a dam and reservoir to support hydroelectric power takes a lot of money, time, and construction. Moreover, hydroelectricity is hydrology dependent which the system depends on precipitation levels that can fluctuate from year to year, causing instability. Therefore, water energy harvesting technologies are complex and expensive that encourages researchers to invent new technology for exploiting water energy into electricity.

## 2.2 Overview of chitosan

Chitosan is a natural polymer which has a linear chain with poly-D-glucosamine (composed of randomly distributed more than 5000 units of glucosamine and acetylglucosamine) and molecular weight more than one million Dalton. Chitosan was discovered by C. Rouget when he heated chitin to the boiling point in a concentrated KOH solution which followed by Rigby that contributed to the formation of making films from chitosan fibre in 1934 (Dutta et al., 2004). Until now, chitosan is highly researched and developed not only in the industrial field but in fields whose applications are for society at large. This development is not only due to the availability of chitosan which is abundant in nature, but because of the existence of amine and hydroxy groups that can be utilized as needed (Ma and Sahai, 2013; Chupp et al., 2015)

Chitosan is the sixth important compound, and its volume in production in nature ranked the second after collagen (Bansal et al., 2011). Chitosan is naturally abundant and available from many kinds of organism, especially from crustacean shells: from industrial food waste, crustacean shells which are estimated to have a total volume of sea creatures more than 100 million tons per year (Rinaudo, 2006).

Generally, in order to manufacture chitosan, the synthesis process comprises the steps of deproteinization, demineralization, decolouring and deacetylation. Since chitin is available abundantly, chitosan is produced cheaply. Chitin is described as a precursor for the manufacture of chitosan, which has a difference in the size of the degree of deacetylation (DD) while chitosan is known to have 80% - 90% DD. The chemical chain or structure of chitin and chitosan can be seen in Figure 2.9. Because of particular conditions which used during the process of deacetylation, chitosan has a shorter chemical chain than chitin which commonly dissolved in acetic acid.